

Laser hybrid fabrication of nanoporous structures on metallic material surface

Yide KAN, Yu GU, Changsheng DONG, Minlin ZHONG, Wenjin LIU, Mingxing MA, Hongjun ZHANG

*Key Laboratory for Advanced Materials Processing Technology, Ministry of Education,
Laser Processing Research Center, Department of Mechanical Engineering, Tsinghua University,
Beijing, 100084, China
E-mail: zhml@tsinghua.edu.cn*

This paper reports a novel approach to fabricate Cu-Mn nanoporous structures by laser deposition hybrid with electrolyte dealloying. Cu₂₅Mn₇₅ alloy layers free of cracks were fabricated by laser deposition onto a mild steel surface. The dendrite microstructure of the as-deposited layer was further processed by laser remelting to refine the grain size and change the morphology to be cellular crystalline. Electrolyte dealloying was then applied on the as-deposited and remelted layers. Uniform porous microstructure will form under optimized electrode current density to be about 5 mA/cm². The size of the porous structure decreases with the increase of laser remelting speed. Nanoporous structure is available with remelting speed up to 83 mm/s. A minimum size of nanoporous structure was achieved to be 35.2 nm up to date with this laser dealloying hybrid method. The Nanoporous Cu-Mn structure was further electrolessly plated of Ni to form a nanoporous Cu-Ni composite coating. The Cyclic voltammetry curves indicate that both the nanoporous Cu coatings and the nanoporous Cu-Ni composite coatings show electrochemical catalysis properties. The Cu-Ni composite coatings with 20 minute Ni plating demonstrates the best catalysis properties, with oxidation peak current density up to about 60 mA/cm².

Keywords: Nanoporous structure, laser deposition, electrochemical catalysis properties

1. Introduction

Nanoporous metals exhibit novel physical and chemical properties, showing a promising potential for scientific research and engineering applications such as catalyst, electrochemical catalysis, detecting, sensing and so on^[1, 2]. Dealloying is considered an effective method to yield nanoporous metals, by which one or more elements are selectively chemically or electrochemically etched from the matrix owing to their high reactivity. This causes structural instability and results in porosity^[3]. In order to achieve dealloying or selective dissolution, two criteria about the chemical potential difference and composition limit must be satisfied. One element of the alloy should be more reactive, such as Al, Mn, Zn, Zr, Ni, and the other should be more noble, such as Au, Pt, Cu. The electric potential is controlled to dissolve only the reactive element^[4, 5]. The nano-porous metals are normally made of noble metal films such as Cu-Pt, Ag-Au and Cu-Au, prepared by arc melting, magnetic sputtering and electrodeposit, which limits their application research^[6-12]. Erlebacher^[13] classified that pores were formed because the more noble atoms are chemically driven to aggregate into two-dimensional clusters by a phase separation process at the solid-electrolyte interface.

Cu-Mn binary alloy displays single-phase solid solution across the whole compositional range, and the standard reversible potential difference between Mn and Cu is 1.447V, which provides the maximum flexibility in tailoring the dealloying process. Pryor^[14, 15] studied the dealloying behavior of Cu-Mn alloys. They indicated that the dealloying process involves electrochemical removal of more

electronegative solute atoms from the surface and collapse of residual atoms into equilibrium lattice positions, followed by surface opening up to the solution ingress and pores forming. However, dealloying kinetics and the pore size dependent on the microstructure of the original alloy. Therefore they never obtain nano-structure materials from cold-rolled or annealed Cu-Mn alloys hybridized dealloying process. Because the as-homogenized Cu-Mn alloys by conventional heat treatment consist of manganese-rich and copper-rich region, which is unfavourable for nanostructure forming.

This paper reports a novel approach to fabricate nanoporous copper coatings on mild steel by a two-step process involving high power laser deposition followed by selective anodic etching of the less noble component (Mn) from the alloy. Here, the microstructures of the layers were investigated using SEM, and mercury porosimeter. Polarization of the alloy coatings were investigated using an electrochemical analysis system, and the electrochemical catalysis properties of nano-porous metals was also studied.

2. Experimental Procedure

The mild steel plates in size of 200mm × 50mm × 15mm were used as the substrate in this work. Before laser deposition, the substrate surface was polished using 600 grit metallurgical paper and rinsed with ethanol and acetone. Laser depositing Cu₂₅Mn₇₅(at.%) alloy coatings were conducted using PRC-3000 continuous wave CO₂ laser processing system in argon shielding atmosphere. Laser remelting was carried out at different speed when

Report Documentation Page			Form Approved OMB No. 0704-0188		
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE JUN 2009		2. REPORT TYPE		3. DATES COVERED 00-00-2009 to 00-00-2009	
4. TITLE AND SUBTITLE Laser hybrid fabrication of nanoporous structures on metallic material surface			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Tsinghua University,Key Laboratory for Advanced Materials Processing Technology,Laser Processing Research Center, Department of Mechanical Engineering,Beijing, 100084&#65292;China,			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM002324. Presented at the International Congress on Laser Advanced Materials Processing (5th) (LAMP 2009) Held in Kobe, Japan on June 29-July 2, 2009. Sponsored by AFOSR/AOARD. U.S. Government or Federal Rights License.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 5	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

laser deposited coatings cooled down. The parameters of laser processing were listed in Table 1.

Table 1 Laser processing parameters

Process	Laser power (KW)	Scanning speed (mm/s)	Laser diameter (mm)
Deposition	1.1~1.5	4.0~6.0	2.5~3.0
Remelting	2.0~2.4	30.0~140.0	2.5~3.0

Metallographic cross-sections of samples were prepared perpendicular to the scanning direction. Samples for dealloying were prepared parallel to the surface and along the scanning direction. Then they were polished with 1200 grit abrasive paper. An EG&G 273A Electro-Chemical Comprehensive Test & Measurement System was used in the electrochemical dealloying with a platinum counter cathode and a saturated calomel reference electrode. Dealloying process was conducted in 0.1M HCl aqueous solution about 3 hours at room temperature. After dealloying, the samples were taken out from the electrolyte and rinsed in de-ionized water and acetone. The dealloyed samples were then allowed to air dry.

Electroless plating Ni on nanoporous copper coatings was conducted and ammonia spirit was used in order to adjust the PH value to 7. Electrochemical catalysis properties of the nano-porous coatings was investigated through cyclic voltammetric curves measured by EG&G 273A, with (Ni(OH)₂NiOOH) as auxiliary electrode and a saturated calomel reference electrode. Electrolyte is potassium hydroxide deionized aqueous solution.

The microstructures of dealloyed coatings were characterized using scanning electron microscopy (JSM-6460LV SEM) equipped with X-ray energy dispersive spectroscopy (INCA X-sight 7573 X-EDS). A mercury porosimeter (Auto-pore IV 9510) was used to identify the pore size distribution.

3. Results

3.1 Laser processing

The parameters of laser deposition were optimized to achieve sound Cu-Mn layers with the thickness of 700 μm , free of cracks, pores or inclusion. The dilution was specifically controlled to avoid the designed composition of the Cu-Mn alloy to be modified by the melted Fe from the substrate and thus to obtain a microstructure with a single solid solution, as required to form nano-porous structure by electrolyte dealloying. Microstructure of the deposited layers is characterized typically coarse regular dendrites (Fig.1a).

The dendrite microstructure of the as-deposited layer was further processed by laser remelting to refine the grain size and change the morphology (Fig.1b-d). It is obvious that the deposited microstructure transformed into columnar grain, equiaxed grain, then cellular grain gradually, as the scanning speed or cooling rate increases.

3.2 Electrochemical dealloying

Current density is proportional to the amount of dissolved Mn atoms. The dissolution potential when current density of 5mA/cm² was defined as the critical potential. Electrolyte dealloying was finally preformed on the as-

deposited and remelted layers. Microstructure of electrochemically dealloyed coatings is an interconnected bicontinuous network of pores (fig.2a-d).

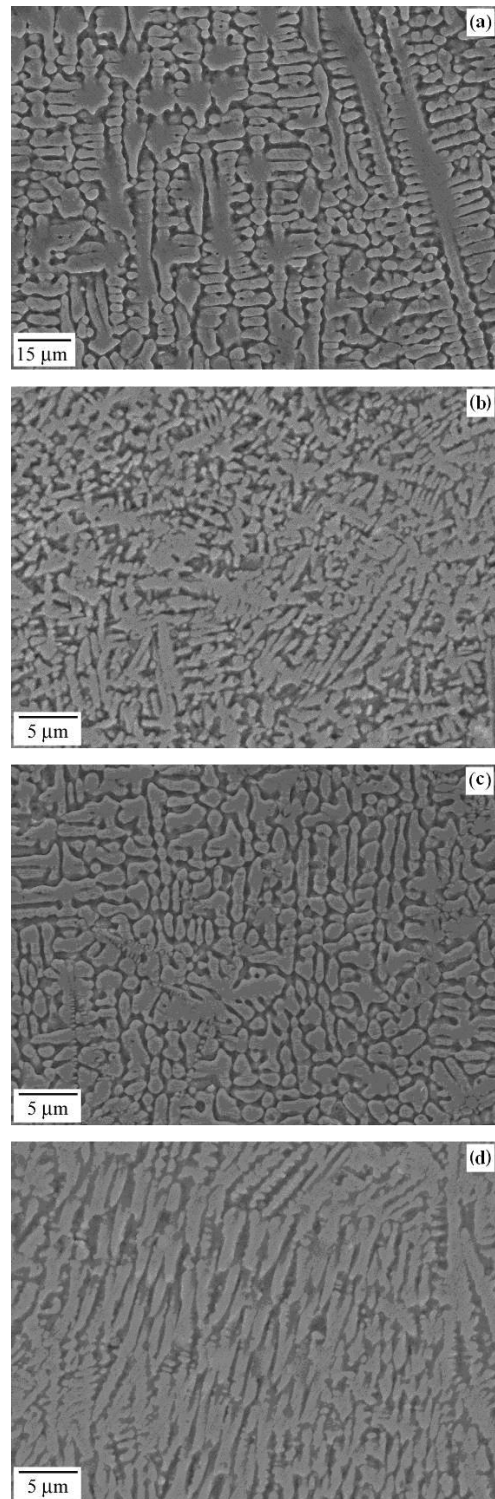


Fig. 1 Microstructure of laser processed Cu-Mn coatings

- a) Microstructure of deposited coatings
- b) Microstructure of remelted coatings at 33mm/s
- c) Microstructure of remelted coatings at 83mm/s
- d) Microstructure of remelted coatings at 133mm/s

Dealloyed as-deposited Cu-Mn alloy layers were characterized an interconnected bicontinuous network. Pores in size of about 500~900 nm formed in this structure. After laser remelting with scanning speed of 33 mm/s, the porous size ranges from 100 to 500 nm. Nano-porous structure is available with remelting speed up to 83 mm/s. The size of nano-porous structure decreases with the increase of laser remelting speed. A minimum size of nano-porous structure is 35 nm up to date with this laser hybrid dealloying method (Fig.2d). The porosity and specific surface area could be as high as 70% and 65.3 m²/g separately.

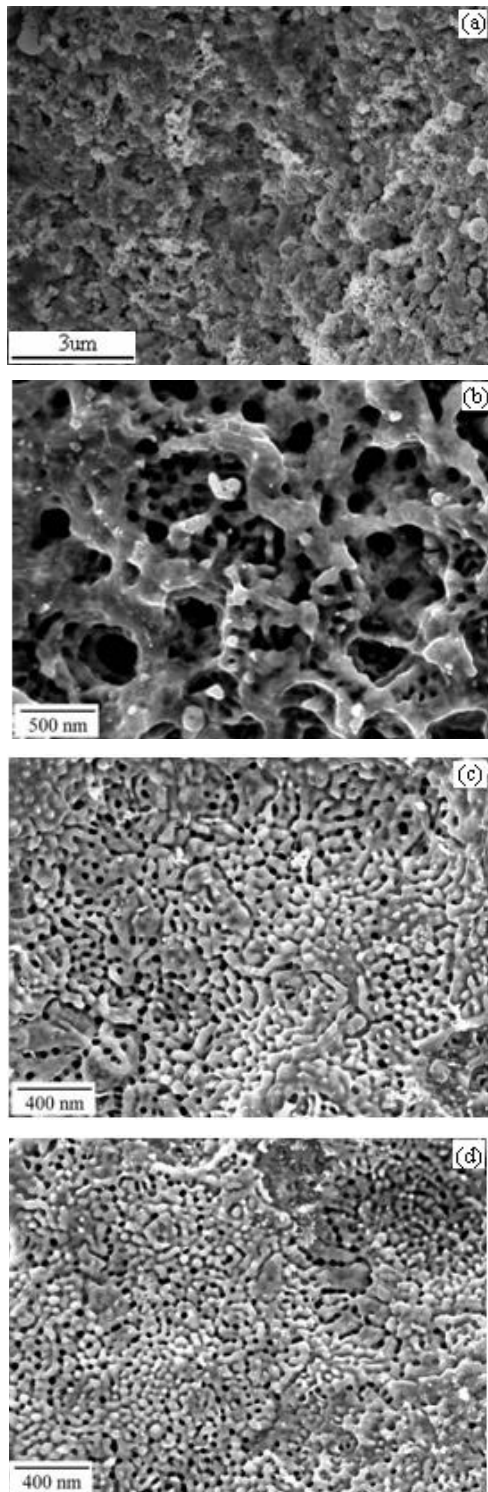


Fig. 2 Microstructure of dealloyed Cu-Mn coatings

(a) Microstructure of dealloyed coatings by laser depositing,
(b)-(d) Microstructure of dealloyed coatings by laser remelting
at 33mm/s, 83mm/s and 133mm/s, separately

The major difference between the dealloyed microstructure of laser depositing coatings and laser remelting ones is attributed to the different microstructure of Cu-Mn coatings. The dealloying process contains dissolution of Mn atoms and surface diffusion of Cu atoms. It has been proven that the initial microstructure of the dealloyed specimen play an important role in microstructure evolution of nano-porous structure during the dealloying process. The key issue to make porous structure is to obtain an appropriate microstructure in which a mechanism exists for the penetration of the electrolyte throughout the alloy, and for the forming of a network of interconnected porous structures. Thus small grain size in the precursor alloys is desirable for the nanoporous structure because it provides a large number of grain boundaries through which the electrolyte can penetrate the alloy [16]. There is another interpretation about the behavior of grain boundary during electrochemical dealloying process. Grain boundary is a more disordered region of atomic arrangement, where the density of crystal defect is abundant. Therefore the potential of grain boundary (vs. SHE) is lower than the internal grain. Dealloying occurs at grain boundary first. When the grain is large and the dendrite grows well, the grain boundary can be fast corrosion paths and thus blocks the homogeneous dealloying, which is unfavorable for the forming of nano-porous structure. Moreover, it has been proposed that the concentration of the active metal is higher in the grain boundary than in the matrix. The grain boundary has greater chemical activity, and would be preferentially attacked in the early stage of corrosion. In another word, ultra-fine grains and homogeneity of the dealloyed alloy significantly balance the dissolution process of more reactive atoms and the rearrangement of more noble atoms, and therefore play a critical role in governing the formation of regularly porous copper. Laser processing offers a promising approach for surface modification due to the ultrafine microstructure and uniform composition. Thus it is easy to understand the pore size decreases as remelting speeding increases.

3.3 Electrochemical Catalysis properties

Nanoporous copper layers with pores ranging from 30 to 50nm have been fabricated by laser deposition of Cu-Mn alloy coatings on mild steel and subsequently dealloying process. In order to achieve electrochemical catalysis properties of nanoporous metal coatings, nanoporous Cu-Ni composite coatings were also obtained after electroless plating of Ni on nanoporous copper (Fig.3a-c). The pore size and specific surface area of the nano-porous Cu-Ni composite coating decreases with the increase of the plating time (Fig.4a-b). There is deficient Ni atomic percentage deposited on the nano-porous copper coatings with electroless plating for only 5 mins. Therefore nickel content is too small to alter the microstructure of nano-porous copper. With electroless plating of Ni for 60 mins, the nickel deposition layer is thick enough to modify nano-porous structure, however the Cu-Ni composite coatings are character-

ized as nano-porous materials with smaller size and smaller specific surface area.

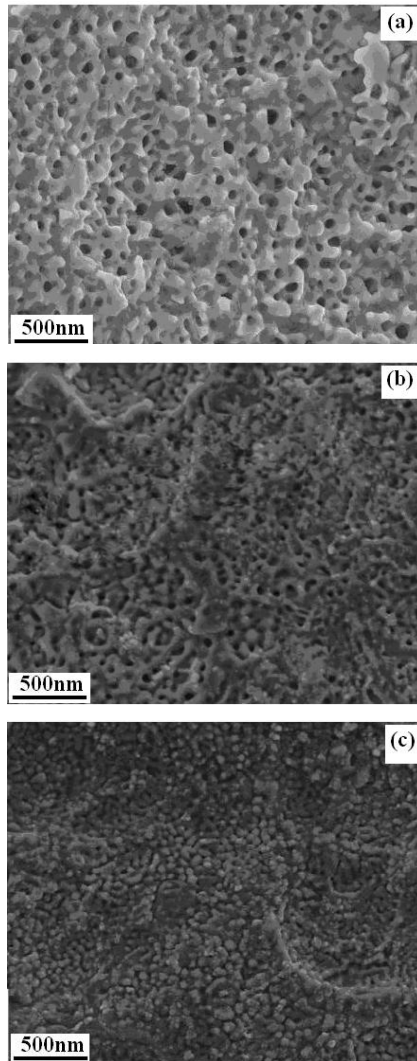


Fig.3 nano-porous Cu-Ni composite coatings

- (a) nanoporous coatings of electroless plating of Ni for 5 min
- (b) nanoporous coatings of electroless plating of Ni for 20 min
- (c) nanoporous coatings of electroless plating of Ni for 60 min

Cyclic voltammetry curves indicate that both nanoporous copper coatings and nanoporous Cu-Ni composite coatings show electrochemical catalysis properties for redox reaction of hydrogen as hydrogen storage electrodes (Fig. 5a-b).

It is well known that hydrogen reduction reaction occurs individually on the surface of polished copper electrode in alkaline solution during electrolytic reaction. While cyclic voltammetry curves of nano-porous copper presents two distinct current peaks, hydrogen reduction peak at -1.10V(vs. Hg/HgO) and hydrogen oxidation peak at -0.44 V(vs. Hg/HgO).

It can be interpreted that nano-porous copper electrode plays an important role to restore the hydrogen generated during electrolytic redox reaction. Furthermore, nanoporous Cu-Ni composite coatings exhibit more excellent electrochemical catalysis performance, as hydrogen restoring electrode. The maximum current density is significantly improved during electrolytic redox reaction when the nano-

porous Cu-Mn composite coatings. Nano-porous Cu-Ni composite coatings with 20 minute Ni plating show the best catalysis properties, with an oxidation peak current density of about 60 mA/cm².

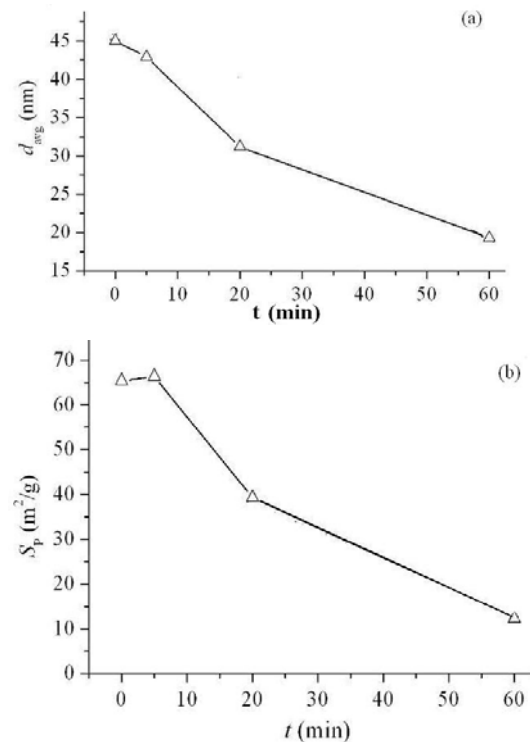


Fig. 4 (a) average pore size; (b) specific surface area of the nanoporous Cu-Ni composite coating

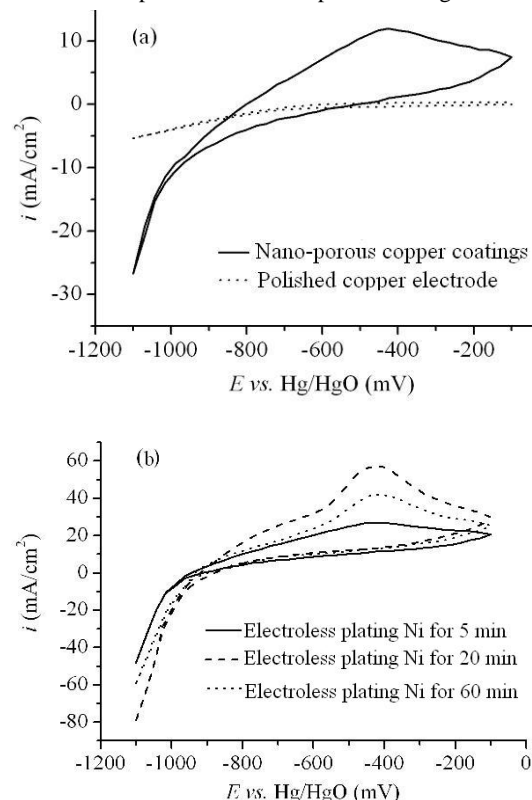


Fig. 5 (a) Cyclic voltammetry curves of nano-porous copper coatings and polished copper electrode
(b) Cyclic voltammetry curves of nano-porous Cu-Mn composite coatings

4. Conclusions

A novel approach to fabricate Cu-Mn nano-porous structures on any location of conventional metallic components is developed by high power laser deposition hybrid with electrolyte dealloying. Cu₂₅Mn₇₅(at.%) alloy layers free of cracks, pores or inclusion were fabricated by laser deposition onto a mild steel surface. The dendrite microstructure of the as-deposited layer was further processed by laser remelting to refine the grain size and change the morphology to be cellular crystalline.

Electrolyte dealloying is applied on the as-deposited and remelted layer controlling current density about 5 mA/cm². Dealloyed as-deposited Cu-Mn alloy layers show porous structure in micrometers. After laser remelting with scanning speed of 33 mm/s, porous structure ranging from 100~500 nm form. Nano porous structure is available with remelting speed up to 83 mm/s. The size of nano porous structure decreases with the increase of laser remelting speed. A minimum size of nano-porous structure is achieved to be 35.2nm up to date with this laser dealloying hybrid method. The porosity and specific surface area could be as high as 70% and 65.3 m²/g separately.

The Nano-porous Cu-Mn structure is electrolessly plated of Ni to form a nano-porous Cu-Ni composite coating, with also high porosity and specific surface area. The pore size and porosity of the nano-porous Cu-Ni composite coating decreases with the increase the plating time. The Cyclic voltammetry curves indicate that both the nano-porous Cu coatings and the nano-porous Cu-Ni composite coatings have electrochemical catalysis properties, which could be used as hydrogen storage electrodes. The composite coatings from Cu₂₅Mn₇₅ nano-porous copper coatings with 20 minute Ni plating have the best catalysis properties, its oxidation peak current density up to about 60 mA/cm².

References

- [1]Thomas K. Hydrogen adsorption and storage on porous materials. *Catalysis Today*, 2007, 120:389-398.
- [2]Haghi A. Transport phenomena in porous media: A review. *Theoretical Foundations of Chemical Engineering*, 2006, 40:14-26
- [3]Hai-Bo Lu, Ying Li and Fu-Hui Wang. Synthesis of porous copper from nanocrystalline two-phase Cu-Zr film by dealloying, *Scripta Material*, 2007, 56: 165-168.
- [4]Un-Sig Min, James C.M. Li. The microstructure and dealloying kinetics of a Cu-Mn alloy, *Journal of material research*,1994, 9:1878-2883.
- [5] Aziz Dursun, Dylan V. Pugh, and Sean G. Corcoran. Probing the Dealloying Critical Potential, *Journal of The Electrochemical Society*, 2005, 152: B65-B72.
- [6]Erlebacher J, Sieradzki K. Pattern formation during dealloying. *Scripta Materialia*, 2003, 49(10): 991-996.
- [7]Zeis R, Tang L , Sieradzki K, et al. Catalytic reduction of oxygen and hydrogen peroxide by nanoporous gold. *Journal of Catalysis*, 2008, 253:132-138.
- [8]Huang J F, Sun I W. Fabrication and surface functionalization of nanoporous gold by electrochemical alloying/dealloying of Au-Zn in an ionic liquid, and the self assembly of L-cysteine monolayers. *Advanced Functional Materials*, 2005, 15: 989-994.
- [9]Jia F, Yu C, Ai Z, et al. Fabrication of nanoporous gold film electrodes with ultrahigh surface area and electrochemical activity. *Chemistry of Materials*, 2007, 19(15): 3648-3653.
- [10]Pugh D, Dursun A, Corcoran S G. Electrochemical and morphological characterization of Pt-Cu dealloying. *Journal of The Electrochemical Society*, 2005, 152(11):B455-B459.
- [11]Jin H J, Kramer D, Ivanisenko Y, et al. Macroscopically strong nanoporous Pt prepared by dealloying. *Advanced Engineering Materials*, 2007, 9(10):849-854.
- [12]Thorp J C, Sieradzki K, Tang L, et al. Formation of nanoporous noble metal thin films by electrochemical dealloying of Pt_xSi_{1-x}. *Applied Physics Letters*, 2006, 88: 033110.
- [13]Erlebacher J, Aziz M J, Karma A, et al. Evolution of nanoporosity in dealloying. *Nature*, 2001, 410(22): 450-453.
- [14]D.S.Kier, M.J. Pryor. The dealloying of the Copper-Manganese Alloys, *Electrochemical Science and Technology*, 1980, 127:2138-2144.
- [15] M.J. Pryor , J.C. Fister. The Mechanism of Dealloying of Copper Solid Solutions and intermetallic Phases, *Electrochemical Science and Technology*, 1984, 131:1230-1235.
- [16] A.J. Smith, D.L. Trimm, Annu. The Preparation of Skeletal Catalysis, *Annual review of materials research*, 2005,35:127-142.